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TECHNICAL REPORT

WHITE OAK LABORATORY

REMOVAL OF TETRANITROMETHANE FROM AIR STREAMS

By
William H. Gilligan
Thomas N. Hall

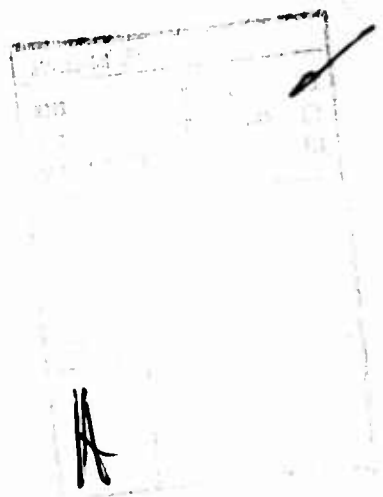8 OCTOBER 1975

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During the manufacture of TNT, one of the side products formed in relatively small amount is tetranitromethane (TNM). In the past it has been the practice to vent the TNM along with some nitrogen oxides (mainly NO) to the atmosphere. However, because of present-day awareness of pollution problems, EPA regulations now require the combined NO/TNM present in the exhaust gases to be below 100 ppm. In order to meet this requirement most of the TNM

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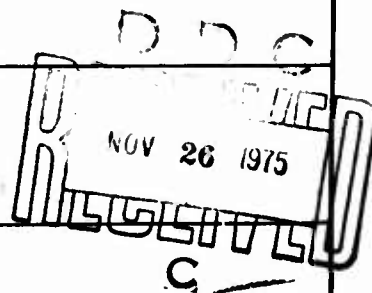
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must be removed. Since TNM as a precursor of nitroform, can be
used for the synthesis of a wide variety of polynitroaliphatics
a desirable solution would be to collect the TNM as such or as
nitroform thereby reducing the cost of pollution abatement. A
gas scrubber was designed and assembled to test the efficiency
of various nucleophiles to remove TNM from gaseous exhausts under
conditions comparable to those found in TNT plants. Good results
have been obtained using alkaline hydrogen peroxide or a two-phase
system of an organic liquid with aqueous alkali as the scrubbing
solution. Laboratory experiments have demonstrated that 90%
conversions are possible. In these scrubbing processes, the TNM
is collected as an aqueous solution of nitroform suitable for sale.

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REMOVAL OF TETRANITROMETHANE FROM AIR STREAMS

Methods have been devised to remove tetranitromethane from TNT
plant exhaust gasses and to convert it to nitroform. A source of
air pollution is thereby eliminated and an important and scarce
chemical intermediate is obtained at a reasonable cost. The work
was funded by the Army's Picatinny Arsenal.

J. Kabek for

JULIUS W. ENIG
By direction

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INTRODUCTION

The Radford Army Ammunition Plant (RAAP) at Radford, Va., manufactures TNT by a process developed by Canadian Industries Ltd. (CIL Process). At Radford there are three continuous lines which can produce 50 tons of TNT per line per day.

During the manufacture of TNT rather large amounts of gaseous side products are formed. The major constituents of these gases are nitrogen oxides (NO_x), with smaller amounts of carbon dioxide, carbon monoxide and tetranitromethane (TNM). At Radford these off-gases are drawn from over the nitration reactors by the application of a partial vacuum and passed through four 24' x 4' steel counter-current wash towers, the first three of which contain water and the last concentrated sulfuric acid. The effluent gases from the last wash tower contain 300 - 400 ppm (v/v) of TNM and a 100 ppm (v/v) of NO_x, consisting mainly of nitric oxide (NO), which are then vented to the atmosphere at a rate of 700 to 900 ft^3 per minute. In addition a smaller untreated exhaust system vents approximately 1000 ppm (v/v) of TNM at the rate of 300 - 450 ft^3 per minute. It is estimated that the average amount of TNM discharged to the atmosphere would be about 500,000 lbs per 3 lines per year.

Recently Radford has been advised by the Environmental Protection Agency (EPA) that the total emission of NO_x including TNM, could not be greater than 100 ppm. This new standard necessitates the almost complete removal of TNM from the exhaust gasses. Since TNM is a precursor of nitroform, a valuable and expensive intermediate used for the synthesis of a wide variety of polynitroaliphatics, a desirable solution would be to collect the TNM as such or as nitroform thereby reducing the cost of pollution abatement.

RESULTS AND DISCUSSION

A number of possible methods for the removal of TNM can be envisioned. However, the simplest and most directly applicable appeared to be by the use of aqueous solutions of nucleophiles as scrubbers to continuously remove TNM from an air stream and concurrently convert it to nitroform. After the nitroform had reached a practical concentration it could then be removed for sale. To test the feasibility of such a process a laboratory scrubber was constructed (Figure 1) to conform in scale to those in use at RAAP. In general the operating conditions (air flow, TNM concentration) were chosen to conform to the extreme or near-extreme that would likely be encountered in practice.

Table 1 lists the rate constants for the reaction of a number of nucleophiles with TNM. Assuming that the faster the reaction rate the more efficient the nucleophile will be as a scavenger, the most

TABLE 1

Rates of Reaction of Some Nucleophiles with TNM (Aqueous Solution)

Nucleophile	k_2, M^{-1} MIN^{-1}
Alkaline Peroxide	66,000[1]
Na_2SO_3 (Sellite)	9,000[4]
$Na_2S_2O_3$	63[3]
NaOH	39[2]
$NaNO_2$	3.6[3]
NaI	3.4[3]
NaN_3	3.3[3]
NaSCN	1.9[3]
NaCN	1.2[3]

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1. W. S. Sager and J. C. Hoffsommer, J. Phys. Chem., 73, 4155 (1969)

2. D. J. Glover, J. Phys. Chem., 74, 21 (1970).

3. S. L. Walters and T. C. Bruice, J. Am. Chem. Soc., 93, 2296 (1971)

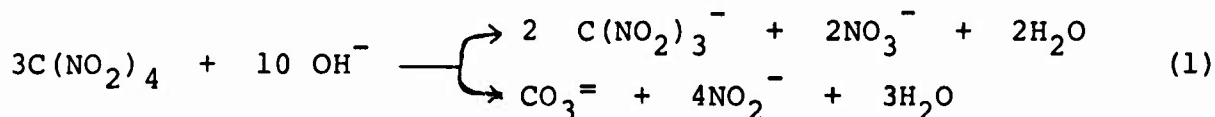4. L. A. Kaplan, Private Communication.

effective should be alkaline peroxide. However, since hydrogen
peroxide decomposes quite rapidly in alkaline solution it was
initially discounted as a practical choice. Later it was found that
commercially available preparations of stabilized hydrogen peroxide
decomposed much less rapidly and could be used as TNM scavengers.

Initial experiments with aqueous solutions of sodium sulfite
(sellite) showed that it was an effective scavenger for the removal
of TNM from air streams, but since nitroform is not stable in the
presence of excess sulfite it cannot be used where the recovery of
nitroform is desired. Similarly nitroform is not stable in the
presence of excess thiosulfate.

Of the remaining nucleophiles the best choice appeared to be
sodium hydroxide since there are one or more major disadvantages
(low reaction rate, cost, toxicity, etc.) associated with the others.

However, there is also one intrinsic drawback to the use of
sodium hydroxide solutions to convert TNM into nitroform:
Approximately one-third of the TNM is converted to carbonate via a
side-reaction[1].

$$3C(NO_2)_4 + 10 \ OH^- \longrightarrow \begin{cases} 2 \ C(NO_2)_3^- + 2NO_3^- + 2H_2O \\ CO_3^= + 4NO_2^- + 3H_2O \end{cases} \quad (1)$$

In addition to these pathways there is an additional slower reaction
of TNM with nitrite ion (2). The net effect is that

$$C(NO_2)_4 + NO_2^- \longrightarrow C(NO_2)_3^- + N_2O_4$$

$$N_2O_4 + 2OH^- \longrightarrow NO_2^- + NO_3^- + H_2O \quad (2)$$
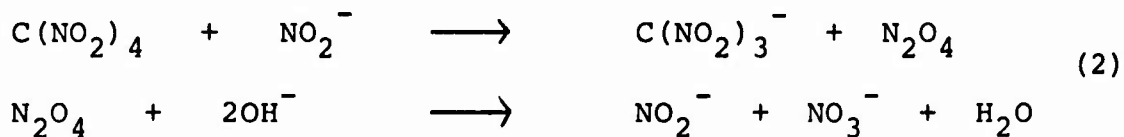
the maximum attainable yield of nitroform will be considerably less
than theoretical; > 75%, < 80%.

Presented in Table II are the results obtained with some aqueous
sodium hydroxide solutions of varying concentration. At the higher
hydroxide concentrations (6N, 4N) the efficiency of removal of TNM
was only 5-11% and varying the liquid cycle rate from 200 to 910 cc/
min had little or no effect. As the hydroxide concentration decreased
there was an increase in the efficiency, which could be further
increased either by increasing the liquid cycle rate or by decreasing
the air flow. It was tentatively concluded from these runs and
confirmed in later experiments that a strong "salt effect" was
operative at the higher concentrations. Presumably, the efficiency
was lowered because of a lowered solubility of the TNM in the aqueous

---

1. D. J. Glover, J. Phys. Chem., 72, 1402 (1968); 74, 21 (1970).

TABLE 2

Effect of OH⁻ Concentration on Efficiency

Run #[a]	NaOH, N	Air Flow, CFH	LCR[b], cc/min	% EFF
1	6.18	12	200	5
2	4.33	6	200	11
8	1.04	6	430	34
10,11	4.18	6	430	8
12	4.20	6	910	8
13	1.05	6	910	50
14	0.41	6	910	54
15	1.03	4.2	910	71

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a) The time period for these runs was 6 to 7 hours. The average TNM concentration was 410 ppm (v/v) ± 10 ppm.

b) LCR - liquid cycle rate.

phase. It appeared then that sodium hydroxide solutions would be of little practical value as TNM scrubbers.

It was now clear that either the solubility of TNM or its reaction rate would have to be increased or alternatively a faster reacting nucleophile would have to be used. In a paper by Findler and Liechti[2,3] it was claimed that small concentrations of hexadecyltri-methylammonium bromide (HTMAB) enhanced the rate constant for the reaction of hydroxide ion with TNM by a factor of 400. However, under our conditions at a 1N sodium hydroxide concentration, nitroform was precipitated from the scrubber solution during the course of a run as the hexadecyltrimethylammonium salt. Any effect of the HTMAB on the reaction rate was therefore short-lived.

Pursuing this line of investigation, the effect of a number of other surfactants of differing types on the scrubbing efficiency was investigated, Table 3. Of these, only Brij 92, a polyoxyethylene oleyl ether, showed a significant improvement in efficiency (54 to 86%). In the presence of added salts, Brij 92 raised the efficiency from 32 to 55%. While such a system presumably could be used for the recovery of nitroform, more than one scrubbing tower would be required which would increase initial costs.

Walters and Bruice[4] have studied the reactions of alkoxide ions with TNM in aqueous alcohol solutions. They found that the formation of nitroform was due largely to the reaction of alkoxide ions rather than hydroxide ions. The reaction of primary alkoxide ions was quite clean, the only discernible products being nitroform and alkyl nitrate. This rate enhancement coupled with an increased solubility

$$RCH_2O^- \quad + \quad C(NO_2)_4 \quad \longrightarrow \quad C(NO_2)_3^- \quad + \quad RCH_2ONO_2 \quad (3)$$

of TNM in aqueous solutions of organic additives would presumably raise the scavenging efficiency. In Table 4 are given the results of some runs with diethylene glycol, ethylene glycol and bis (methoxy) ethyl ether. As expected, the efficiency was raised from 54% to 67-80%. Again, the presence of salts caused a sharp drop. There appears to be little advantage to be gained by the additives tested and there are the disadvantages of cost and the possible formation of unstable nitrate esters.

2. J. H. Findler and R. R. Liechti, J. Chem. Soc., (Perkin II) 1041 (1972).
3. We thank Dr. Everett Gilbert of Picatinny Arsenal, Dover, NJ, for bringing our attention to this paper.
4. S. L. Walters and T. M. Bruice, J. Am. Chem. Soc., 93, 2269 (1971).

TABLE 3

Effect of Surfactants on Efficiency

Run #[a]	NaOH, N	Air Flow, CFH	LCR, cc/min	Additive	% Eff
8	1.04	6	430	--	34
9	1.04	6	430	0.1% Tide	37
13	1.05	6	910	--	50
16	1.06	6	810[b]	1% Daxad	55
17	1.05	4.6	500[b]	0.5% Santomerse S	57
18	1.03	---	---[c,b]	0.5% Na Lauryl Sulfate	--
20	1.04	4.6	910	0.5% Sterox Se	58
14	0.41	6	910	--	54
22	0.54	6	910	0.5% Brij 92	86
23	0.50	6	910	1% Brij 92	83
30	0.50	6	910	0.2% FC 98	57
35	0.50	6	910	1% DMOD	65
33&34	0.50	6	910	29% Salts[d]	32
32	0.50	6	910	29% Salts[d] + 0.9% Brij 92	55

a) The time period for these runs was 6 to 7 hrs. TNM conc. was
   410± 10 ppm.
b) The liquid cycle rate (LCR) had to be lowered because of foaming.
c) Foaming was so excessive the experiment was discontinued.
d) 14% sodium nitrite, 8.7% sodium nitrate, 3.9% sodium carbonate.

TABLE 4

Effect of Organic Solvents on Efficiency

Run #[a]	NaOH, N	Additive	% Eff.
14	0.41	----	54
19	0.49	11% Diethylene glycol	80
21	0.61	5.6% Diethylene glycol	67
24	0.54	5% Bis(methoxy)ethyl ether	70
25	0.49	5.6% ethylene glycol	73
37	1.50	----	45
27	1.64	29% salts[b] + 5.8% ethylene glycol	27
28	1.50	29% salts[b] + 15.1% ethylene glycol	68
29	1.50	29% salts[b] + 15.1% ethylene glycol + 0.8% Brij 92	65

a) Liquid Cycle Rate was 910 ccs/min; air flow 6 cfh; TNM - 410 $\pm$ 10 ppm; time 6-7 hrs.
b) Sodium nitrite 12%, sodium nitrate 7.4%, sodium carbonate 2.8%.

One possible way to avoid salt effects is by the use of organic aqueous "emulsions". In such a system, the TNM would be soluble in the organic phase and yet would be in close contact with the aqueous solution of the nucleophile. A high molecular weight alcohol appeared to be worthy of consideration as the organic phase for several reasons: a) the polar group would aid in emulsification, b) it was considered probable that there would be a significant concentration of alkoxide ion at the organic-aqueous interface and therefore the bulk of the reaction would take place in the organic phase with the attendant effects of lower salt concentration and an increased yield of nitroform, c) the cost of the aliphatic alcohols is low and would be more than compensated for by the increased yield of nitro-form.

Our choice of n-octanol as the organic phase was dictated by its availability at the time the experiments were carried out; however, either decanol or dodecanol or mixtures thereof would have the advantage of lower volatility. In Table 5 are given the results using two-phase mixtures of n-octanol and aqueous sodium hydroxide. In run #41 the aqueous phase contained 39% salts and was continued for 6 hrs. The average TNM concentration was 430 ppm (v/v) which was higher than the usual 410. Both the efficiency and the yield were essentially quantitative indicating that indeed the reaction was occurring in the organic phase and that the effect of the dissolved salts was negligible.

Run #47 (Table 5) was designed to simulate actual operating conditions for an extended period of time. The run was continued for 114 consecutive hrs. The final concentration of sodium nitroform was 22.3%. The overall yield was 90%. However the circulating pump for the scrubber reservoir stopped sometime during the last 17 hrs of operation. An unknown amount of TNM was lost during that period. The 90% yield figure is then a minimum value.

TABLE 5

Effect of Two-Phase Systems on Efficiency

Run #[a]	NaOH, N	Salt, %	Organic Additive	Eff., %
41	0.6	39[b]	50 ml n-octanol + 0.25% Daxad 11	102
47	1.0	---	55 ml n-octanol + 0.25 g Daxad 11	90

a) LCR- ?!0 cc/min; air flow 6 cfh; aqueous phase 210cc.
b) Sodium nitrite 16.5%; sodium nitrate 20.2%.

An aliquot of the organic phase was taken each day during the five (5) days of operation for an estimation of the octyl nitrate content. This increased linearly with time during the first four days but for the last 17 hour period there was a sharp drop in the rate of octyl nitrate formation. Since the octyl nitrate is hydrolytically stable under these conditions, this is a good indication that the true yield figure for this run should approach 100%.

Some concern has been expressed that the presence of an alkyl nitrate could be an explosion hazard. In view of the low oxidant balance, the general stability of n-alkyl mononitrates, other than the methyl, and the presence of an excess of water acting as a heat sink this concern appears unwarranted.

The reaction of TNM with alkaline hydrogen peroxide has long been used as a preparative method for nitroform[5,6] (equation (4)). However, because of the instability of hydrogen peroxide under alkaline conditions it was believed that it would be too costly to be

$$C(NO_2)_4 + 2OH^- + H_2O_2 \longrightarrow C(NO_2)_3^- + O_2 + 2H_2O + NO_2^- \quad (4)$$

used as a scavenger for TNM. While this investigation was underway we learned that stabilized solutions of hydrogen peroxide were available from Du Pont under the trademark Albone.[7] These preparations were designed for bleaching operations under mild alkaline conditions and conceivably could make practical the use of alkaline peroxide as a TNM scrubber.

An initial study of the stability of Albone DS 50 (50% H_2O_2 by wt) under our experimental conditions showed that the rate of decomposition was proportional to the hydroxide concentration and the half-life was inversely proportional to the initial peroxide concentration in the concentration range studied (0.1 to 1.5 M). This indicated that the concentrations of both alkali and peroxide should be as low as possible to avoid waste.

In Table 6 are given the results of some runs using both stabilized and unstabilized hydrogen peroxide under various conditions of alkalinity. With unstabilized peroxide, run #31, the yield of nitroform was 76% which was fairly low considering that a 1300% excess of peroxide was used. This is undoubtedly due to the rapid decomposition of peroxide during the run. With stabilized peroxide, the results were quite promising. A yield of 93% was obtained either with or without added salts, runs #55 and 63. When sodium carbonate was substituted for sodium hydroxide there was a decrease in the yield to 81% which was further decreased to 67% when sodium bicarbonate was used as the alkalizing agent. Again, these results point up the need for close control of pH.

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5. Schimmelschmidt, Hunter Report, B105 1919/22 1G July 3, 1946.
6. K. Klager and M. B. Frankel, Aerojet Report No. 494, 13 Feb 1951.
7. The stabilizer used in these solutions is magnesium sulfate.

When a long term run[8] was attempted the results became quite erratic on a day to day basis. The yields ranged from a high of 98% to a low which was negative. During this extended run, despite the fluctuation in the yield the efficiency approached 100% since very little nitroform was evident in an alcoholic KOH trap through which the exhaust air was passed before venting. An analysis of the scrubber solution after 80 hrs of operation showed that the nitrite concentration was 1.8 times that of the nitroform. There was very little nitrate ion present. This was a strong indication that a part (~20%) of the nitroform had been completely decomposed to nitrite and presumably sodium carbonate.

TABLE ᴄ

Alkaline Hydrogen Peroxide vs Yield %

Run #[a]	Conditions	% Yield
31	0.5 N NaOH, 13 ml 30% H_2O_2; after 3 hrs 10 ml more	76
55	0.2 N NaOH, 3 ml Albone DS 50	93
58	0.45 N Na_2CO_3, 3 ml Albone DS 50	81
60	0.2 N $NaHCO_3$, 3 ml Albone DS 50	67
63	0.3 N NaOH, 4 ml Albone DS 50, 40% Salts[b]	93

a) time - 6 hr runs; LCR - 910 cc/min; Air flow - 6 cfh; TNM conc. - 410 ± 10 ppm (v/v).
b) Sodium nitrate 21%; sodium nitrite 18%.

This conclusion was confirmed by adding excess peroxide (stabilized) to solutions of sodium nitroform (0.91 M) containing sodium hydroxide (1.0 M), sodium carbonate (1.0 M) and sodium bicarbonate (1.0 M). In 48 hrs there was 25%, 4%, and 89% decomposition respectively. It would appear that nitroform is most stable at or around pH 10.5, in the presence of hydrogen peroxide.

The finding that nitroform is subject to decomposition was not anticipated. On the contrary, the consensus had been that nitroform was stable under these conditions. Obviously a careful investigation of the rates of decomposition under closely controlled conditions is desirable. Such an investigation however, is outside the scope of this study. Nevertheless, the use of alkaline peroxide as a scrubber to remove and convert TNM into nitroform appears to be practical if close attention is paid to the operating conditions.

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8. For this extended run the scrubber was in operation for 6 to 7.5 hrs/day and then shut down during the night. Thus, the nitroform was in contact with alkaline peroxide for much longer periods than would be the case in actual practice.

Inorganic ions unavoidably contaminate the nitroform solutions produced by all of the TNM scavenging solutions studied. These nitroform solutions can be used directly to prepare derivatives of nitroform such as trinitroethanol. For example, a 96% yield of trinitroethanol was obtained from one such solution by acidification, addition of formaldehyde, and extraction with methylene chloride in the usual manner[6]. The inorganic contamination is undesirable for some nitroform applications, but can be eliminated by distilling the nitroform under reduced pressure, after acidification in the presence of a nitrous acid scavenger[9]. Thus, it does not appear that any undue problems will be encountered in the utilization of the nitroform solutions produced by the scavenging of TNM from air streams.

9.   G. A. Wetterholm & E. L. Nilson, US Patent 2,658,084 (1953).

EXPERIMENTAL

The scrubber (Figure 1) consisted of a glass cylinder 2 inches in diameter X 24 inches in length and was packed with 1/4" pyrex helices to a height of 13 inches. The bottom tapered to a 24/20 $ joint to which a 300 ml 3 neck flask was connected. The flask served as a reservoir for the scrubber solution and was connected by Tygon tubing to a variable speed pump and thence to a glass showerhead which was positioned over the column packing. Tetranitromethane (TNM) was introduced into the main air stream by diverting a measured portion of air through a bubbler containing the TNM. The bubbler was weighed at the beginning and end of each run to determine the total amount of TNM passed into the scrubber. The air stream containing the TNM entered the scrubber at a point about one inch from the bottom of the packing. Nitric oxide could be added to the air stream in a similar manner. The air flow and the TNM concentration were adjustable by means of valves incorporated in the flowmeters. The liquid cycle rate was monitored by means of a flowmeter and was adjusted by varying the pump speed.

At the end of each run the concentration of nitroform in the scrubber liquid was determined by measuring the absorbance at 350 mu with a Model 14 Cary spectrophotometer. A molar absorption value of 14,950 was used.

The efficiency of a run was defined as the percentage of the TNM which was removed from the air stream. For alkaline peroxide solutions and for two-phase alcohol/hydroxide systems this was considered to be the same as the yield[10]. For aqueous hydroxide solutions the efficiency was taken as 1.5 times the yield. And, for one-phase alcohol/hydroxide solutions the efficiency was calculated as the % yield of nitroform due to the alkoxide reaction plus 1.5 times the % yield of nitroform due to the hydroxide reaction as calculated according to the method of Walters and Bruice[4].

Nitrite and Nitrate Ions

Nitrite and nitrate ions were determined by the method of English as modified by D. J. Glover.[1,11]

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10. This is not accurate for alkaline-peroxide solutions since as is shown in the text peroxide solution can attack nitroform. However, for runs of short duration it approaches the true value.
11. F. L. English, Ind. Eng. Chem. Anal. Ed., 19, 850 (1947).

Surfactants

The following surfactants were tested for effectiveness in the course of this study. "Daxad 11", a polyalkylnapthalene sulfonic acid (sodium salt), Dewey and Almy Co., Cambridge, Mass., "Santomerse 5", a mixture of alkyl aryl sulfonates, Monsanto Corp., St. Louis, Mo., "Sterox SE", a polyoxyethylene thio ether, Monsanto Corp., "Deysonol", sodium lauryl sulfate, DuPont, Wilmington, Del., "Brij 92", polyoxyethylene(2)oleyl ether, Atlas, Wilmington, Del., "FC 98", anionic fluorocarbon, 3 M Co., St. Paul, Minn., DMOD, 3,6-dimethyl-octyne-3,6-diol.

Distillation of Nitroform from Nitroform - Salt Solutions[8]

To 350 ml of an aqueous solution containing 83.13 g (0.551 mol) of nitroform (as the sodium salt), 29.2 g (0.275 mol) of sodium carbonate, 47.0 g (0.555 mol) of sodium nitrate and 70.0 g (1.02 mol) of sodium nitrite was added 72.0 g (1.20 mol) of urea. The solution was cooled in an ice bath and 170 ml of 50% sulfuric acid (1.5 mol) was added dropwise with efficient stirring at such a rate that the temperature of the solution was maintained at or below 15°C. During the addition a slow stream of air was passed over the surface of the solution to dissipate nitrogen oxides.

After addition of the acid the solution was distilled through a short, unpacked column, fitted with a claisen distillation head, into a cooled receiver containing 100 mg of urea at a pressure of 100 to 120 mm. After rinsing the condenser and head, and combining the rinses with the distillate, 420 ml of solution was obtained which contained 75.20 g of essentially pure nitroform. The recovery was 94.1%.

Trinitroethanol from Nitroform/Salt Solution

To 110 ml of an aqueous solution containing 33.25 g (0.22 mol) of nitroform as the sodium sodium salt, 11.66 g (0.11 mol) of sodium carbonate, 18.78 g (0.22 mol) of sodium nitrate and 28.00 g (0.41 mol) of sodium nitrite was added 12.0 g (0.2 mol) of urea. After cooling in an ice bath, a solution of 34 ml (0.6 mol) of conc. sulfuric acid in 100 ml of water was added dropwise with efficient stirring while maintaining the temperature at or below 14°. After addition of the acid, 20 ml of 36% formalin was added and the solution stirred for 15 min. The mixture was then extracted with methylene chloride and the extracts dried by azeotropic distillation. The methylene chloride solution was then filtered and the solvent removed in vacuo. The product consisting of small white crystals weighed 38.5 g (96.6%), the purity of the product by GLC was 99%.
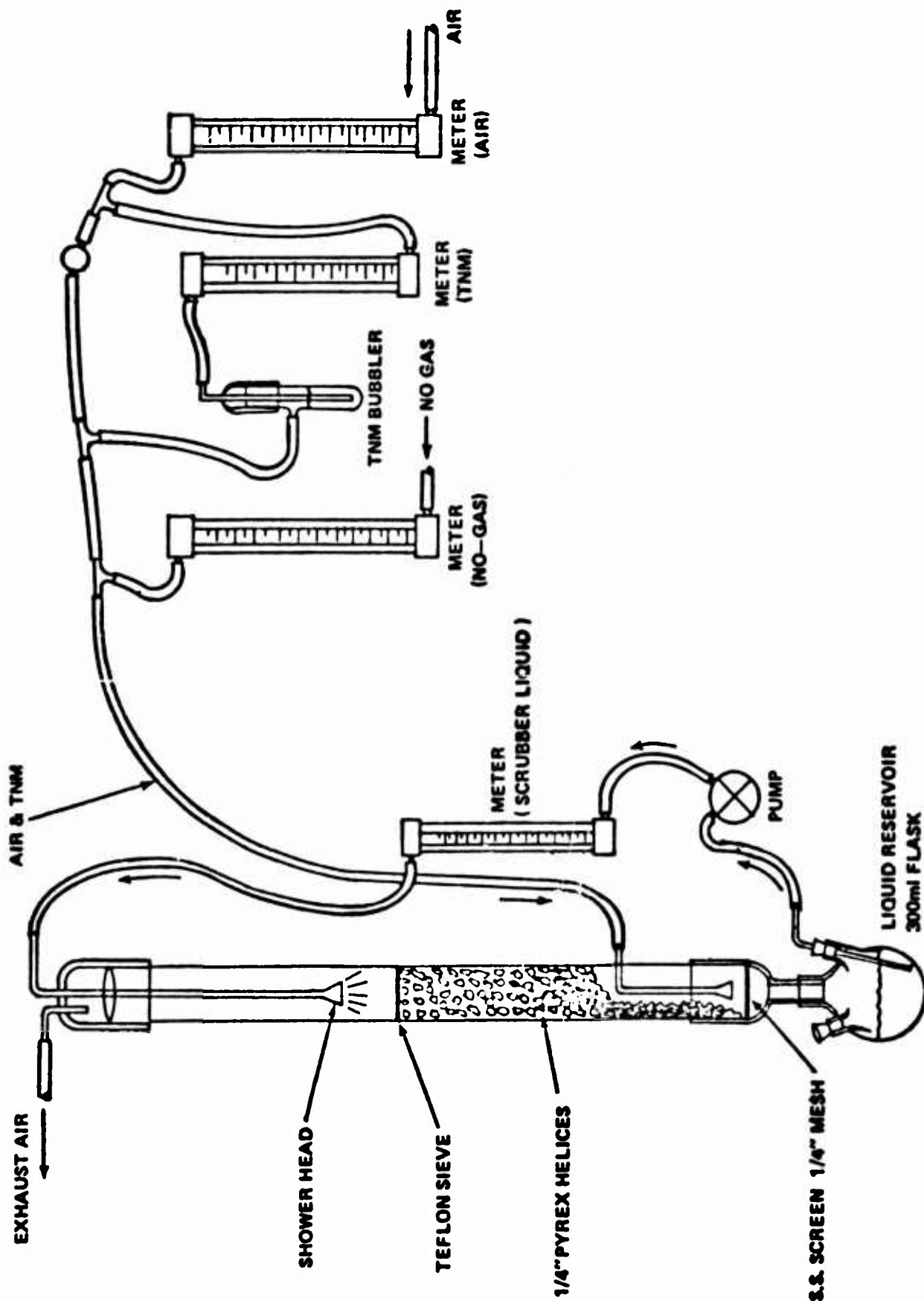
FIG. 1 TNM SCRUBBER

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